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(54) Title: LOW CALORIC FAT SUBSTITUTES, PRECURSORS OF SUCH SUBSTITUTES AND METHODS OF MAKING SAME

(57) Abstract

A new linear polyglycerol composition, a method of making the composition and novel low caloric fat substitutes derived by esterification of the polyglycerol composition is described. Optionally, the polyglycerol composition is capped with an alkylene oxide prior to esterification. The polyglycerol has a narrow molecular weight distribution, is low in odor and color and has mostly secondary or tertiary hydroxyl groups.

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LOW CALORIC FAT SUBSTITUTES, PRECURSORS OF SUCH
SUBSTITUTES AND METHODS OF MAKING SAME

The invention is related to low caloric oil or fat substitutes and processes for making the low caloric oil or fat substitute.

5 There are numerous reasons for reducing calorie or fat intake. Although fats provide essential nutrients, they have been linked to certain chronic diseases such as arteriosclerosis, heart disease, cancer and obesity. Thus, by reducing the amount of fat and 10 calories in an individual's diet, the risk of disease may also be reduced.

It would be advantageous to be able to replace 15 fat substances with a material that has reduced calories, without losing the properties which make 20 desirable. Desirable properties attributable to fats include the richness in taste or textural characteristics that are associated with certain foods. It is important that these and other organoleptic properties associated with fats are maintained.

A major portion of natural edible oils are triglycerides, which are the triesters of glycerine and 25

various fatty acids. The organoleptic characteristics which we associate with an oil depend upon the fatty acids of the triglycerides. The fatty acids may be saturated, unsaturated, cyclic, acyclic, oxygenated or non-oxygenated.

5 The chemical and physical properties of a triglyceride are largely determined by component fatty acids. Since there are numerous fatty acid groups, there is significant variation in physical and chemical properties of regular oils, e.g., color, viscosity, 10 flash point, smell and the like. Thus, the properties of a fat substitute can be controlled by the choice of fatty acid groups comprising the oil.

15 Other important attributes in a fat substitute are that it should be thermally stable under intended conditions, be safe to consume, and be minimally absorbed through the digestive tract. A significant problem with many of the previously developed fat 20 substitutes is that they cause anal leakage or diarrhea.

One proposed fat substitute is sucrose polyester (SPE), U.S. Patent 3,600,186 to Mattson et. al. and U.S. Patent 3,963,699 to Rizzal et al. The process for making SPE requires a long reaction time with alternating additions of fresh transesterification catalyst and excess methyl soybean fatty acid ester (RCO_2Me). The processing steps are time consuming and increase operating costs.

30 In Rizzal's patent, SPE is prepared by solvent free interesterification using phenyl esters. Phenol is liberated during the process. A preparation process in

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which phenol is liberated is not generally attractive to the food industry.

An alternative to SPE is esterified epoxide-extended polyols (EEEP) as fat substitutes as taught in European Patent Application 87306468.7. The fat
5 substitutes are prepared by treating polyols in the presence of a base catalyst with an epoxide to produce epoxide-extended polyols (EEP). The EEP is reacted with at least one fatty acid to produce an epoxide-extended
10 polyol esters. Every hydroxyl group on the polyol is replaced with an ether linkage. The end groups may be either secondary or primary and are esterified.

It would be desirable to provide a new
15 composition that is a precursor for a low caloric substitute for edible oil or fat that may be easily and economically reacted to produce a low caloric oil or fat substitute, wherein said oil/fat substitute is substantially not hydrolyzed by or absorbed by mammalian
20 digestive processes. Said oil/fat substitute additionally should be produced using a wide variety of fatty acids to achieve desirable properties such as color, taste, mouthfeel without generating toxicity or adverse physiological difficulties upon consumption.
25

The invention is a linear polyglycerol composition that is a precursor for making a low caloric oil or fat substitute, said precursor having a high level of hydroxyl functionality permitting, upon further
30 processing, esterification with a wide variety of fatty acids whereas an oil/fat substitute is achieved having a high content of secondary and tertiary esters which minimizes hydrolyzation or absorption by a mammal but

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enhances or retains desirable characteristics of an oil or fat.

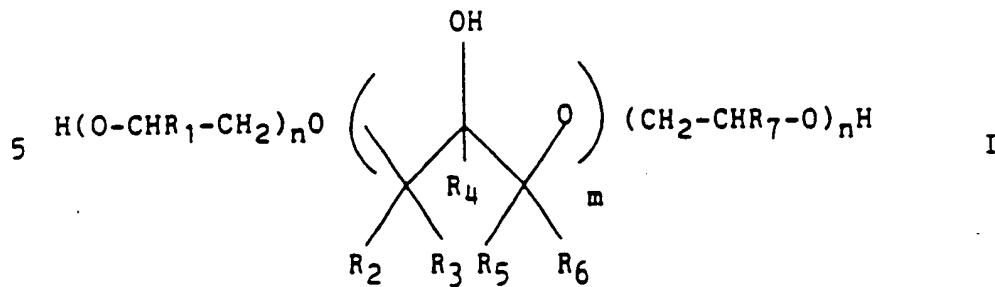
The present invention is also a linear polyglycerol composition that has been esterified to produce a low caloric fat substitute. The invention is 5 also a method of making the polyglycerol composition. This low caloric fat substitute is made by the esterification of a polyglycerol that is enriched in secondary and tertiary hydroxyls. The polyglycerol is prepared by polymerizing glycidol in such a manner that 10 a linear molecule is made. The polyglycerol may also be reacted further with an alkylene oxide before esterification to further enhance secondary and tertiary ester content.

15 This polyglycerol has a narrow molecular weight distribution without further processing; is low in odor and color; and has greater than 50 percent of the hydroxyls present as secondary or tertiary groups.

20 Preferably to maximize the secondary or tertiary ester links in the low caloric fat substitute, the linear polyglycerol is reacted with an oxide having 3 to 6 carbon atoms prior to esterification. By linear it is meant that the polyglycerol is linear if 50 percent or 25 less of its hydroxyl groups are primary groups. Preferably, the polyglycerol has less than 40 percent of its hydroxyl groups primary, more preferably, less than 30 percent.

30 The linear polyglycerol composition of the invention corresponds to Formula I:

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10

where m is an integer from 2 to 30 inclusive, R_1 and R_7 are each independently alkyl groups of 1 to 4 carbon atoms, n is an integer from 0 to 32 inclusive, and R_2 , R_3 , R_4 , R_5 and R_6 are each independently selected from hydrogen or an alkyl group having 1 to 3 carbon atoms and the composition is at least 50 weight percent linear polyglycerol moieties and contains less than 20 weight percent of compounds wherein m is 3 or less.

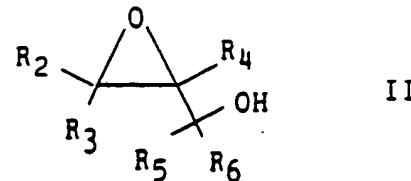
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The polyglycerol is made by heating a basic catalyst and an initiator with agitation to a temperature in the range from 25° to 130°. The initiator is selected from the group consisting of sugars, sugar alcohols, dihydroxy alcohol, polyhydroxy alcohol, 25 polyether polyols, metal alkoxides or metal hydroxides. Preferred are sodium or potassium salts of methanol, ethanol, 1-propanol or sodium or potassium hydroxides. Glycerine is the preferred initiator.

30

A monomer is added to the catalyst and initiator at a rate such that the temperature is maintained between 100° to 160°C. The monomer is of the general Formula II:

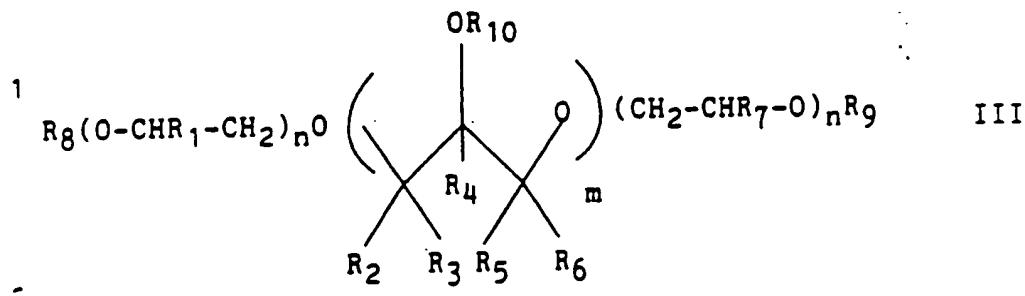
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5

and R₂, R₃, R₄, R₅ and R₆ are each independently hydrogen or an alkyl group having 1 to 3 carbon atoms.

As stated previously the polyglycerol can be
10 esterified to produce a low caloric fat substitute
represented by the following Formula III:



m is 2 to 30 inclusive, R₁ and R₇ are each independently alkyl groups of 1 to 4 carbon atoms, n is an integer from zero to 32 inclusive, and R₂, R₃, R₄ R₅ and R₆ are each independently hydrogen or an alkyl group having 1 to 3 carbon atoms, and R₈, R₉ and R₁₀ are each independently acyl groups having 5 to 23 carbon atoms.
25 After consumption by a mammal, at least 50 percent of the fat substitute is recoverable in the mammal's feces.
30 Preferably 60 to 100 percent of the fat substitute is recovered in the feces. More preferably 70 to 100 percent of the fat substitute is recovered in the feces.

In mammals it is thought that triglycerides are initially hydrolyzed at the primary esters and absorbed in the body. It is now believed that the reason for the high level of recovery of the polyglycerol fat substitute of the invention in feces of animals following ingestion is due to the relatively high content of secondary and tertiary esters. Additionally, the molecular weight of the composition is a factor which contributes to the body's inability to absorb the fat substitute. An important benefit to having a high level of hydroxyl functionality is that there is more flexibility when making the fat substitute. The hydrogen of the hydroxyl group can be replaced with an acyl group to form an ester. The acyl group is preferably derived from a fatty acid. By choosing the appropriate fatty acids in appropriate proportions, such properties as the melting point, the stability, as well as other properties of the fat substitute, e.g., viscosity, taste, mouthfeel, color etc., are controlled. This gives flexibility in producing a fat substitute that has desirable physical and chemical properties.

These fat substitutes are useful to replace fats or oils in many different types of foods. The fat substitute is useful as a cooking oil, in margarine spreads, baked goods and baking mixes, confections, frostings, salad dressings, frozen desserts and mixes, puddings and hard and soft candies. Fat is also absorbed by foods while frying. The snack industry uses a large amount of fats and oils in the production of potato chips, corn chips and other snack items. A low calorie fat substitute that has acceptable oil

properties could be useful for producing such snacks, thereby producing a low calorie snack.

In addition to these polyglycerols being used to make fat substitutes, they could also be employed in a number of other food applications. For example, the 5 polyglycerol has a high viscosity so it could be used to improve the viscosity of the low calorie beverages and soft drinks. The high viscosity and water solubility make it useful for applications which employ gum acacia. Due to the chemical stability and high viscosity of the 10 polyglycerol, it can also be useful in acidic food preparations such as pickle relish, ketchup, citrus juices and the like.

15 There are many advantages of this process of making polyglycerol over other processes practiced in the art. For instance, there is no need for removal of a solvent, nor is there a need for purification of the resulting product. The yields are very good, generally 20 nearly quantitative. The polyglycerol has a low color and odor content. The process affords excellent molecular weight control, meaning greater than 80 percent of the polyglycerol has the targeted molecular weight. Additionally, when compared with polyglycerols 25 produced by other processes, the resulting polyglycerol has a narrow molecular weight distribution. Also, when compared with polyglycerols prepared by other processes, there are low levels of residual glycerine or oligomers 30 in the polyglycerol, and the process results in a polyglycerol uniquely enriched in secondary and tertiary hydroxyl content.

The linear polyglycerol compound that has at least two secondary or tertiary hydroxyl groups is

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represented by Formula I. Preferably the glycerine units are from 70 to 80 weight percent of the polyglycerol composition. More preferably, the glycerine units are greater than 80 percent of the polyglycerol composition. In Formula I, preferably, m is 6 to 15 glycerine units, more preferably m is 8 to 12 glycerine units; R₁ and R₇ are preferably each independently an alkyl group of 1 to 3 carbon atoms, more preferably 1 or 2 carbon atoms; n is preferably an integer from 1 to 15 inclusive, more preferably, 1 to 5 inclusive. R₂, R₃, R₄ R₅ and R₆ are preferably each independently a methyl group, an ethyl group or hydrogen.

When m is 6 or greater, there may be a minor amount of lower molecular weight polyglycerol compounds present. Advantageously less than 1 to 20 weight percent oligomers, preferably less than 1 to 10 weight percent oligomers, more preferably less than 5 weight percent oligomers, are present in the composition. By oligomers it is meant a polyglycerol having 3 or less repeating units of glycerine, that is, m is 1, 2 or 3.

The low calorie fat substitute can be made by substantially complete esterification of the above described linear polyglycerol. The low caloric fat substitute is represented by Formula III hereinbefore.

In Formula III, m is an integer preferably from 6 to 15 inclusive, more preferably 8 to 12 inclusive. R₂, R₃, R₄, R₅ and R₆ are each independently hydrogen or an alkyl group having 1 to 3 carbon atoms, preferably a methyl or ethyl group or hydrogen. R₈, R₉ and R₁₀ are acyl groups having from 5 to 23 carbon atoms. The acyl group can advantageously be derived from the fatty acids

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found in common edible oils, including olive oil, soybean oil, coconut oil, palm oil, cotton seed oil and canola oil. These fatty acids may include oleic, octanoic, lauric, eicosanoic, stearic, palmitic, linoleic, myristic acid, and linolenic acids or the acyl group could be derived from a complex mixture of these fatty acids. Additionally, the acyl group is in one preferred embodiment derived from mixtures of natural oils that could be short, medium, or long chain, saturated or unsaturated, cis or trans. Examples of 5 short chain acyl derived from shorter chain aliphatic acids which could include, but are not limited to valeric, hexanoic, or octanoic acids. Medium chain acyl group could be, but is not limited to caproic, caprylic, capric, lauroleic, lauric, and caproleic acid, decenoic, 10 and ethanoic. Long chain acyl groups include but are not limited to behenic, lignoceric, arachidic, myristoleic, palmitoleic, gadoleic, erucic, elaidic, vaccenic, archidonic, and eicosapentaenoic acid. The 15 acyl group is preferably derived from one or more fatty acid types, and most preferably is derived from a complex mixture of the fatty acids that are derived from 20 natural oils.

Another aspect of this invention is the method 25 of making the linear polyglycerol. The linear polyglycerol is made under conditions that are generally anhydrous. By "generally anhydrous" is meant that minor amounts of water can be present in glycerine, glycidol 30 or the atmosphere, so long as the water does not adversely affect the desired reaction. Glycerine is reacted with glycidol to form a linear polyglycerol. To achieve the most favorable results, glycerine is mixed neat r solvent free with glycidol under anhydrous

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conditions. The presence of water or a polar or protic solvent capable of hydrogen bonding generally has adverse effects upon the polymerization of polyglycerol. These adverse effects may include an increase in the primary hydroxyl content, an increase in the percentage of lower oligomers, broad molecular weight distribution, 5 and inhibition of chain extension of the polyglycerol.

In addition to certain solvents having an adverse effect upon the polymerization of glycerol, the 10 concentration of glycidol, even though it is a reactant, could have an adverse effect upon the reaction. It is important that the concentration of glycidol be controlled such that there is no build-up of glycidol in the reactor. It is not advantageous to have excess 15 unreacted glycerine in the presence of the polyglycerol, because it is theorized that the unreacted glycerine will be converted to triglycerides upon esterification of the polyglycerol. Since triglycerides are hydrolyzed 20 in the small intestines, the triglycerides can increase the caloric content of the oil.

Another condition which could also result in loss of selectivity is inefficient mixing or stirring of the mixture. Stirring is important, because it is 25 necessary that glycidol be distributed uniformly throughout the mixture. Efficient stirring also affects the heat transfer within the mixture.

More specifically to make a linear 30 polyglycerol, glycerine and a base catalyst are heated with agitation, preferably in the absence of water and oxygen. The basic catalyst can be lithium; sodium; rubidium; magnesium; cesium; metal hydroxides such as sodium hydroxide, calcium hydroxide, and barium

hydroxide; metal hydrides such as sodium, potassium, lithium, and calcium hydride, lithium aluminum hydride, sodium borohydride; sodium carbonate; sodium amide or sodium sulfate. Preferably, the catalyst is potassium metal, sodium metal, sodium hydroxide, potassium hydroxide, calcium hydroxide or barium hydroxide. The amount of catalyst heated with the glycerine, based on the amount of glycerine employed, is 0.001 mole percent to 10 mole percent, preferably 0.5 to 10 mole percent, more preferably 1 mole percent to 5 mole percent. The quantity of catalyst may affect the color of the resulting polyglycerol, since generally the more catalyst used the darker the color of the polyglycerol.

The glycerine and catalyst are preferably heated under nitrogen to a temperature in the range from 25° to 130°C. Agitation is desirable from about 40 to about 130°C. Glycidol is added slowly to the glycerine. Optionally, glycidol is added to the glycerine below the liquid surface. The addition is carried out in such a manner that the temperature during addition is maintained between 100° to 160°C. After the addition of the glycidol is completed, the mixture is heated at a temperature from 100° to 160°C, preferably 115° to 125°C for a period of up to about 16 hours, preferably for about 3 to about 6 hours. Most preferably, the mixture is heated at about 120° to 125°C for about one hour.

Also, it is preferred that the catalyst is added to the glycerine and nitrogen introduction is discontinued when the mixture reaches 60°C. If the glycidol is added too rapidly, the polyglycerol's secondary or tertiary hydroxyl content will be affected,

along with the molecular weight and molecular weight distribution of the polyglycerol.

The stoichiometric ratio of glycidol to glycerine determines the polymer chain length. To make a diglycerol with a molecular weight of 166, a mole ratio of glycidol to glycerine of 4:1 to 1:1 is advantageous, preferably about a 2:1 ratio is employed. To make a triglycerol with a molecular weight of 240, a mole ratio of glycidol to glycerine of 6:1 to 2:1 is advantageous, preferably about a 4:1 ratio. To make a tetraglycerol with a molecular weight of 314, a mole ratio of glycidol to glycerine of 9:1 to 3:1 is advantageous, preferably a 6:1 ratio. To make a pentaglycerol with a molecular weight of 388, a mole ratio of glycidol to glycerine of 11:1 to 4:1 is advantageous, preferably a 7:1 ratio. To make a hexaglycerol with a molecular weight of 462, a mole ratio of glycidol to glycerine of 14:1 to 5:1 is advantageous, preferably a 9:1 ratio. To make a octaglycerol with a molecular weight of 610, a mole ratio of glycidol to glycerine of 19:1 to 7:1 is advantageous, preferably a 12:1 ratio. To make a nonaglycerol with a molecular weight of 684, a mole ratio of glycidol to glycerine of 22:1 to 8:1 is advantageous, preferably a 14:1 ratio. To make a decaglycerol with a molecular weight of 758, a mole ratio of glycidol to glycerine of 24:1 to 9:1 is advantageous, preferably a 16:1 ratio.

By producing a polyglycerol that has a high molecular weight, the ester derivatives of the polyglycerol are expected to be less susceptible to enzymatic hydrolysis and absorption, although a lower molecular weight linear polyglycerol might be useful in

applications which the high molecular weights are not desirous. Additionally, the molecular weight of the polyglycerol will depend on whether a diglycerol, triglycerol, tetraglycerol and the like are produced. The higher molecular weight polyglycerols are preferred for the preparation of a low caloric fat substitute.

5 The molecular weight distribution is also important, since the presence of lower molecular weight oligomers may affect the over all performance of the derived polyglycerol oils as low caloric fat substitutes.

10 Generally any conventional means of esterifying the polyglycerol is operable to produce the low caloric fat substitute. The polyglycerol may be transesterified by using one of the transesterification catalysts known in the art. Examples of such catalysts include organic titanates, organic acids, or mineral acids. Typically, esterification of the polyglycerol is accomplished by stirring the polyglycerol with a catalyst used in esterification processes such as, pyridine, cyclohexyl-20 -carbodiimide or p-toluene sulfonic acid at 15°C to 60°C, preferably from 20°C to 40°C. A fatty acid or a fatty acid equivalent, that is, a fatty acyl halide, an ester of fatty acid, or a fatty acyl anhydride is added to the polyglycerol mixture, and these reactants have the acyl group corresponding to R₈, R₉ and R₁₀. Alternatively, the polyglycerol may be esterified with a low molecular weight acyl halide or equivalent and then the ester groups exchanged with an excess of fatty acid. A 25 solvent may be added at any time, to aid in the proper mixing of the reaction mixture. If a solvent is added, any non-polar, aprotic solvent may be used. However, hydrocarbon solvents, such as hexane, are preferred.

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The resulting unpurified oil can be filtered and extracted with any number of polar solvents. Water, ethanol, methanol, isopropanol or any combination of these is preferred. Salts such as sodium chloride, potassium chloride or alkaline materials such as sodium hydroxide, potassium hydroxide may be added to the aqueous extracting phase to aid in extraction of free fatty acids and separation of phases. The solvent may be removed from the oil by a number of means, but is conveniently done in the laboratory using a rotary evaporator. The oil can be deodorized if desired by steam stripping or treated further in any manner that normal oils are treated. Additives may or may not be added, as thought necessary.

After the polyglycerol is made, it is esterified with a fatty acid acyl derivative to produce the low caloric fat substitute. The resulting low caloric fat substitute, if diglycerol tetraoleate, has a molecular weight of 1226. Triglycerols esterified result in triglycerol pentaoleate having a molecular weight of 1565; tetraglycerol results in tetraglycerol hexaoleate having a molecular weight of 1904; pentaglycerol results in pentaglycerol septaoleate having a molecular weight of 2242; hexaglycerol results in hexaglycerol octaoleate having a molecular weight of 2582; octaglycerol results in an octaglycerol decaoleate having a molecular weight of 3260; and nonaglycerol results in a nonaglycerol undecaoleate having a molecular weight of 3599.

In a preferred embodiment, in order to assure the polymerization of a polyglycerol having high secondary or tertiary content greater than about 85 percent, the polyglycerol is "capped" or reacted with an

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oxide under alkaline conditions. By capping the polyglycerol the existing primary hydroxyls become secondary or tertiary hydroxyls. The oxides which can be employed to cap the polyglycerol have the following formula:

5



10 where R is an alkyl group. Preferably, the R is methyl, ethyl or propyl. More preferably, the polyglycerol is reacted with propylene oxide, and most preferably polyglycerol is reacted with butylene oxide.

15 To cap the polyglycerol, the polyglycerol is stirred with a catalyst, preferably as nitrogen is flushed through the system. The catalyst is similar to the catalyst used herein to make the polyglycerol. Gradually, the temperature is raised from 20°C to 110°C, 20 preferably 20° to 100°C, then the oxide is slowly added to the polyglycerol and reacted until the oxide vapor pressure ceases to drop. After reacting the polyglycerol with the oxide the resulting compound can be esterified to form the low calorie oil. The crude 25 capped oil can be further processed or cleaned-up if so desired, by the procedures discussed herein for uncapped crude oils.

To cap a diglycerol with a molecular weight of 30 166, a mole ratio of polyglycerol to oxide respectively of 1:0.01 to 1:4 ratio is advantageous, preferably a 1:2 ratio is employed. To cap a triglycerol with a molecular weight of 240, a mole ratio of 1:0.1 to 1:4 ratio is advantageous, preferably a 1:2 ratio is

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employed. To cap a tetraglycerol with a molecular weight of 314, a 1:0.1 to a 1:6 is advantageous, preferably a 1:2 ratio is employed. To cap a pentaglycerol with a molecular weight of 388, a mole ratio of 1:0.1 to 1:7 is advantageous, preferably a 1:3 ratio is employed. To cap a hexaglycerol with a molecular weight of 462, a mole ratio of 1:0.1 to 1:8 is advantageous, preferably 1:3 ratio is employed. To cap a 5 octaglycerol with a molecular weight of 610, a mole ratio of 1:0.1 to 1:10 is advantageous, preferably a 1:3 ratio is employed. To cap a nonaglycerol with a molecular weight of 684, a mole ratio of 1:0.1 to 1:11 is advantageous, preferably a 1:3 ratio is employed. To cap a decaglycerol with a molecular weight of 758, a 10 mole ratio of 1:0.1 to 1:12 is advantageous, preferably a 1:3 ratio is employed. 15

The capped polyglycerol can be esterified as described herein for uncapped polyglycerol to produce the low caloric oil.

20 The following examples are meant to be illustrations of the invention, but are not meant to be limitations thereto.

25 EXAMPLES

¹³C NMR Determination of Percent Secondary Hydroxyls

Polyglycerol samples were dissolved in D₂O/acetone-d₆ with added tetramethylsilane (TMS) and 30 scanned on either a JEOL GX-270 or an IBM NR80 NMR. A 45° pulse with a 10-second pulse delay was used and scans were accumulated overnight. Peak assignments were made based on a model equation for calculating resonances in ¹³C NMR spectra. In later experiments

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chromium acetylacetone (CrAcac) was added, in lieu of the 10-second pulse delay, in order to suppress the nuclear-Overhauser effect.

Pretreatment Steps for Glycidol and Potassium Metal Prior to Making polyglycerol

5 Glycidol was distilled at 42°C, under 2 mm of Hg. Potassium metal that was stored in mineral oil, was rinsed with hexane before being weighed into a tared beaker of mineral oil, rinsed with hexane and dried under a stream of nitrogen before being added to
10 glycerine.

Example 1 - KOH Catalyzed, Glycerine Initiated Synthesis of Hexaglycerol with 70 Percent Secondary Hydroxyls via Anhydrous Glycidol Polymerization

15 A three-neck round-bottom flask (50 ml) was charged with 3.15 g (0.034 mol) of glycerine and 0.120 g of 87 percent pure potassium hydroxide (1.86 mmol of assay). The mixture was stirred and heated under nitrogen to approximately 80°C. At this point a high
20 vacuum (0.5 mm Hg) was applied and the mixture was heated for an additional 30 minutes. The vacuum was then removed and the nitrogen pad was restored, taking care to ensure that the atmosphere inside the flask
25 remained dry. The homogeneous mixture was heated to 115°C and 20.75 ml (0.313 mol) of glycidol was added dropwise through a constant addition funnel. The addition was carried out in such a manner that the temperature was maintained between 115° and 125°C. After
30 the glycidol addition was complete, the mixture was heated at 115°C for one hour. On cooling, a light brown viscous material was obtained. The resulting material was analyzed using gas chromatography for the presence of unreacted glycidol, gel permeation for determining

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molecular weight and a ^{13}C nuclear magnetic resonance (NMR) for secondary hydroxyl content.

Analysis

Gas Chromatograph

5 Gas chromatographic analysis failed to detect glycidol.

Gel Permeation Chromatograph

10 Glycerine, diglycerol and hexaglycerol were used as standards to calibrate the gel permeation chromatography (GPC). Then the following polyglycerols as described below were made according to the above-described procedure in Example 1 and their molecular weights were determined using the calibrated GPC. The 15 results of the analyses are given below.

Mz = 838 (undecaglycerol)

Mw = 658 (nonaglycerol)

20 Mn = 463 (hexaglycerol)

^{13}C Nuclear Magnetic Resonance (NMR)

The theoretical value of hexaglycerol is 75 percent secondary hydroxyls. To determine the 25 percent secondary hydroxyls of the hexaglycerol made in Example 1, analysis of the resulting material was done via ^{13}C NMR. It was determined that the resulting material had 70 percent secondary hydroxyl content.

30 Example 2 - KOH Catalyzed, Glycerine Initiated Synthesis of Hexaglycerol With 71 Percent Secondary Hydroxyls Via Anhydrous Polymerization of Glycidol

A 250 ml round-bottom flask was charged with 20.10 g (0.218 mol) of 99+ percent glycerine and 0.680 g

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of 87 percent pure potassium hydroxide KOH (10.5 mmol of assay). The mixture was heated under vacuum (approximately 60°C, 1.5 mm Hg) for one hour. At the end of this period the vacuum was released and a nitrogen pad provided. The homogeneous mixture was heated to 115°C. Glycidol (167.2 mL 2.52 mol) was added, dropwise, through a constant addition funnel to the mixture. The glycidol addition rate was adjusted so that the temperature was kept within the range of 115° to 125°C (about 0.2 ml/minute). After the addition was complete the mixture was stirred at 110°C for an additional 12-hour period. The addition took 15 hours and 15 minutes. The polymer was a light brown viscous material at room temperature. The molecular weight and secondary hydroxyl content are given below.

Mz = 746 (decaglycerol)
Mw = 624 (octaglycerol)
Mn = 468 (hexaglycerol)
percent secondary hydroxyl = 71 percent

Example 3 - Potassium Metal Catalyzed, Glycerine Initiated Synthesis of Nonaglycerol with 76 Percent Secondary Hydroxyls via Anhydrous Glycidol Polymerization

Potassium metal (0.85 g, 0.0217 mol) and glycerine (20.0 g, 0.217 mol) were mixed in a nitrogen atmosphere. The temperature was raised from 23°C to 123°C over a 3 hour period. Glycidol (241.47 g, 3.26 mol) was added at 0.4 mL/min. After all the glycidol was added, it was stirred for 6 hours. The pH of the polyol mixture was adjusted to 6 from 11 with phosphoric acid. The polymer had a molecular weight of 700, with 93 percent f the theoretical number (9) of secondary hydroxyls. The yield of recoverable

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polyglycerol was 261 g or 99.5 percent. The percent secondary hydroxyls is 76 percent.

Example 4 - Potassium Metal Catalyzed, Glycerine Initiated Synthesis of Pentaglycerol with 64 Percent Secondary Hydroxyls via Anhydrous Glycidol Polymerization

5 Glycerine (108.8 g, 1.18 mol) was stirred with potassium metal (0.93 g, 0.024 mol) under nitrogen. The mixture was heated gradually to 123°C. Glycidol was added at a rate of approximately 0.4 mL/min (474.52 g, 6.4 mol). The mixture was stirred at 123°C for 12 hours
10 after all of the glycidol had been added. The molecular weight was determined to be 414.7. The yield of recoverable polyglycerol after transferral was, 581 g or 99.5 percent. The percent of secondary hydroxyls in the
15 pentaglycerol is 64.

Example 5 - Potassium Metal Catalyzed, Glycerine Initiated Synthesis of Undecaglycerol with 76 Percent Secondary Hydroxyls via Anhydrous Glycidol Polymerization

20 Glycerine (25.59 g, 0.278 mol) was stirred with 0.59 g (0.015 mol) of potassium metal at 45°C for two hours. The mixture was gradually heated to 123°C and glycidol (433.2 g, 5.84 mol) was added at a rate of 0.3 mL/min. The mixture was heated for 15 hours after
25 all of the glycidol had been added. The brown polymer had a molecular weight (M_n) of 839. The yield of recoverable polyglycerol after transferral was 457 g or 99.5 percent. The percent of secondary hydroxyls in
30 undecaglycerol is 76.

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Example 6 - Potassium Metal Catalyzed, Glycerine
Initiated Synthesis of Decaglycerol with
73 Percent Secondary Hydroxyls via Anhydrous
Glycidol Polymerization

Potassium (0.57 g, 0.0146 mol) was added to glycerine (24.94 g, 0.271 mol) and the mixture stirred at 50°C. The temperature was gradually raised to 125°C, 5 at which point glycidol (302.14 g, 4.08 mol) was added at a rate of 0.3 mL/min. The polymer was stirred for 5 and 1/2 hours after the addition was completed. The polymer was analyzed to have a molecular weight of 753. 10 The yield of recoverable polyglycerol after transfer was 328 g or 99.5 percent. The percent of secondary hydroxyls in decaglycerol is 73.

Example 7 - Potassium Metal Catalyzed, Glycerine
Initiated Synthesis of Nonaglycerol with
73 Percent Secondary Hydroxyls via Anhydrous
Glycidol Polymerization

In a 500 mL tapered flask, glycerine (25.53 g, 0.277 mol) and potassium (0.58 g, 0.015 mol) was stirred at 50°C for 30 minutes, 70°C for 30 minutes, and 90°C for 20 2 and 1/2 hours. The temperature was then raised to 120°C and 311.1 g of glycidol was added at a rate of 0.4 mL/min. A one-hour digestion time was observed after complete addition of glycidol. The polymer had a 25 molecular weight of 652, with 73 percent secondary hydroxyls. The yield of recoverable polyglycerol after transferal was, 335 g or 99.5 percent. The percent of secondary hydroxyls in nonaglycerol is 73.

Example 8 - Potassium Metal Catalyzed, Glycerine
Initiated Synthesis of Nonaglycerol with
75 Percent Secondary Hydroxyls via Anhydrous
Glycidol Polymerization

In a tapered 500 mL flask, glycerine (25.63 g, 0.278 mol) was stirred with 0.55 g (0.014 mol) of potassium metal catalyst. The temperature was gradually

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raised from 23° to 123°C over a 3-hour period. Glycidol (310.8 g, 4.17 mol) was added over a period of 21 and 3/4 hours. A 3-hour digestion period was observed. The polymer had a molecular weight of 702 g. The yield of recoverable polyglycerol after transfer was 260 g or 99.5 percent. The percent of secondary hydroxyls is 75.

5

Example 9 - Potassium Metal Catalyzed, Glycerine Initiated Synthesis of Octaglycerol with 72 Percent Secondary Hydroxyls via Anhydrous Glycidol Polymerization

10 Glycerine, 64.56 g (0.71 mol) was mixed with a potassium metal catalyst under agitation. The temperature was gradually increased from 23° to 123°C over a five-hour period. Glycidol was added at a rate of .45 ml/min. over a period of 19 and 1/2 hours

15 (675.5g, 9.11 mol). The mixture was stirred at 123°C for an additional six hours to ensure complete reaction. 736.36 g of octaglycerol was recovered, or 99.5 percent. The percent secondary hydroxyls is 72.

20 Example 10 - Potassium Metal Catalyzed, Glycerine Initiated Synthesis of Decaglycerol with 75 Percent Secondary Hydroxyls via Anhydrous Glycidol Polymerization

25 Potassium metal (0.2157 g, 5.517 mmol) was stirred with glycerine (20.0 g, 0.217 mmol) under a nitrogen atmosphere at 45°C. The temperature was raised to 75°C and maintained for one hour before being increased to 123°C. Glycidol (241.46 g, 3.26 mol) was added at a rate of 0.3 mL per minute. The mixture

30 stirred for 7 and 1/2 hours after the addition was complete. The polymer was determined to have a molecular weight of 729. The yield of recoverable polyglycerol after transfer was 260 g or 99.5 percent. The percent of secondary hydroxyls is 75.

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Example 11 - Potassium Metal Catalyzed, Glycerine
Initiated Synthesis of Decaglycerol with
76 Percent Secondary Hydroxyls via
Anhydrous Glycidol Polymerization

In a tapered 500 ml flask 25.41 g (0.276 mol) of glycerine was stirred with 0.54 g (13.8 mmol) of potassium metal, under a nitrogen atmosphere, at 45°C. After stirring for 30 minutes, the temperature was raised to 60°C. After 30 minutes, the temperature was raised to 90°C for 15 minutes and then to 120°C. At this temperature under agitation, glycidol (304.86 g, 4.113 mol) was added at a rate of 0.3 mL/minute, using a Milton-Roy mini-pump.

After all of the glycidol had been added, the viscous mixture was stirred for an additional 3 and 1/2 hours at 120°C. The mixture was then made neutral with phosphoric acid and allowed to cool to 70°C before pouring into glass jars for storage. On cooling to room temperature the material was a light brown, very viscous liquid.

20

Molecular Weight Analysis of Example 11:

Mz = 900.5

Mw = 847.4

25

Mn = 790.7

The yield of recoverable polyglycerol after transfer was, 329 g or 99.5 percent. The percent of secondary hydroxyls in decaglycerol is 76.

30

-25-

Example 12 - Potassium Metal Catalyzed, Glycerine
Initiated Synthesis of Decaglycerol with
good Secondary Hydroxyl content via
Anhydrous Glycidol Polymerization

The procedures as described in Example 11 were
followed for Samples A-I in Table I, except for the
5 noted change below.

10

15

20

25

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TABLE I

Sample No.	Temperature (°C)	Addition Rate (mL/min)	Catalyst Level (Mol. percent)	Molecular Weight (Mn)	Percent Sec Hydrox.	Percent of Theor.
A	145	0.3	2.5	718	77	95
B	120	0.3	2.5	729	75	90
C	120	0.4	10.0	700	76	93
D	100	0.4	5.0	732	77	92
E	120	0.6	5.0	681	77	94
F	120	0.3	5.1	791	76	92
G*	120	0.3	5.4	839	74	91
H	120	0.3	5.4	753	74	89
I	120	0.3	5.4	729	73	88

*A glycidol to glycerol ratio of 20 to 1 was used.

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The resulting samples in Table I all have high molecular weight, secondary hydroxyl content and the percent yield, based on the theoretical value, are also good.

ESTERIFICATION OF POLYGLYCEROL PRODUCING A LOW CALORIE OIL

5 The next example illustrates the esterification of a polyglycerol, hexaglycerol to make hexaglycerol octaoleate.

10 Example 13 - Preparation of Hexaglycerol octaoleate from a Polyglycerol Backbone of 70 percent Secondary Hydroxyls by Esterification With Oleoyl Chloride

15 Hexaglycerol, 32.6 grams (g), 0.071 mol, having a molecular weight of Mn = 468.2 and 71 percent secondary hydroxyl content were heated, under nitrogen pad with agitation, to between 45° and 50°C in a flask fitted with a hydrogen chloride scrubber. Distilled oleoyl chloride 163.07 g (0.542 mol) was added to the hexaglycerol at a moderate rate. The mixture was stirred for four hours. The crude oil mixture was diluted with hexanes and then pyridine was added in excess, as determined by the lack of formation of pyridinium hydrochloride. The oil was filtered from the hydrochloride salt and passed through a column containing Dowex WGR™ anion exchange resins, a trademark of The Dow Chemical Company. Excess pyridine was azeotroped off with water during deodorization via steam stripping. In this manner, 127 g of hexaglycerol, having 70 percent secondary hydroxyls, was converted to 603 g of hexaglycerol octaoleate.

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Example 14 - Esterification of Hexaglycerol Backbone Enriched With Secondary Hydroxyls to Give a Hexaglycerol Octaoleate Oil

Hexaglycerol (32.6 g, 0.0706 mol) with 71 percent secondary hydroxyl content was heated in a three-neck flask on a water bath at 45° to 50°C. The 5 flask was fitted with a mechanical stirrer, nitrogen inlet and hydrogen chloride scrubber. Oleoyl chloride (163 g, 0.54 mol) was added to the warmed polymer and the mixture stirred for 4 hours. The oil was diluted with hexane, stirred with alumina, and passed twice 10 through a WGR™ anion exchange resin column. After evaporation of solvent, 105.62 g of the hexaglycerol octaoleate was recovered.

Example 15 - Esterification of Octaglycerol Backbone Enriched With Secondary Hydroxyls to Give an Octaglycerol Decaoleate

Octaglycerol, 188.5g, 0.309 mol, was poured into a flask and stirred with 250 g of pyridine. Oleoyl chloride, 939.4 g (93.12 mol), was dripped slowly into 20 the flask. The mixture was stirred overnight. The pyridinium salt was filtered from the oil and the oil extracted with a mixture of ethanol, water, sodium hydroxide. Residual solvent was stripped from the oil and it was deodorized by steam stripping. 865 Grams of 25 oil was recovered.

Example 16 - Esterification of Nonaglycerol With a Fatty Acid Mixture Using Organic titanates

Nonaglycerol ($M_n=651$) (90.46 g, 0.1405 mol) was 30 poured into a three-neck flask (1000 mL). The flask was fitted with a Dean-Stark trap/condenser, a thermometer and a constant addition funnel. The nonaglycerol was warmed and stirred as toluene was added to the flask and trap. Under a nitrogen purge the catalyst, an organic

-29-

titanate/chelate (1.59 g), was added to the mixture. A fatty acid mixture consisting primarily of oleic, linoleic, stearic, and palmitic acids was added to the polyol (407.83 g, 1.471 mol). The flask and contents were heated to reflux, and water was azeotroped at 5 167°-170°C, over 55 hours (25 mL). The oil was dissolved in hexane and extracted with aqueous NaOH, followed by extraction with hot water to reduce the level of free fatty acids and remove the catalyst. The oil was concentrated by removal of solvent under vacuum, 10 381.34 g was recovered (72.5 percent yield).

Absence of hydroxyl absorption in the infrared spectrum of the polyglycerol oil indicated that the polyol was completely esterified.

15 Example 17 - Esterification of Propoxynonaglycerol With Oleoyl Chloride

Propoxynonaglycerol (549.0 g, 0.716 mol) was stirred with pyridine (630.4 g, 7.98 mol) oleoyl chloride (2393.0 g, 7.95 mol) was added to the mixture. 20 The temperature was kept between 40° to 50°C during the addition. Hexane was added to the stirred suspension. The mixture was stirred for 12 hours after all of the oleoyl chloride was added. The reaction mixture was filtered and the volatiles were removed under reduced pressure. The crude oil was extracted with ethanol to less than one percent free fatty acid. Residual ethanol 25 and other volatiles were removed under reduced pressure.

30 Example 18 - Esterification of Butoxynonaglycerol With Oleoyl Chloride

Butoxynonaglycerol (371.1 g, 0.531 mol) was stirred in a mixture of hexane (1 L) and pyridine (419.49 g, 0.531 mol) at room temperature. Oleoyl

-30-

chloride (1592.7 g, 5.31 mol) was added to the mixture over a 90-minute period. During the addition the temperature of the mixture rose to 75°C. Stirring was continued for 12 hours after the addition was completed. The reaction mixture was filtered and the filter cake washed with hexane. The hexane was combined with the crude oil and the volatiles were stripped on the rotary evaporator. The crude concentrated oil was extracted with ethanol to less than one percent free fatty acid. Volatiles were removed under reduced pressure.

10 Example 19 - Esterification of Butoxynonoglycerol With
Oleoyl Chloride

Butoxynonoglycerol (685.5 g, 0.800 mol) was stirred in a 6 L roundbottom flask with pyridine (705.3 g, 8.93 mol). Oleoyl chloride (2674.9 g, 8.89 mol) was added slowly. The temperature was maintained within 40° to 50°C. Hexane was added to the thick suspension. The mixture was stirred for an additional 15 hours after the acid chloride addition was completed. The pyridinium salt was filtered and the crude oil was concentrated by removal of volatiles under reduced pressure.

25 The crude concentrated oil was extracted with water and ethanol to less than 1 percent free fatty acid. Volatiles were removed under reduced pressure.

Example 20 - Transesterification of Octaglycerol With
Soybean Oil

30 Octaglycerol (50.36 g, 0.0862 mol) was warmed and stirred with 0.3 g of potassium metal, in a three-necked round bottom flask. The flask was fitted with a thermometer, nitrogen inlet, and short path vacuum distillation column. Stirring was continued

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until the metal was completely reacted. Soybean oil (240.0 g) (0.275 mol) was added to the mixture and the temperature was raised to 100°C. Nitrogen purge was stopped and vacuum applied as the temperature was increased steadily to greater than 200°C. Distillate was collected (150°C, 481.3 cm) as the temperature of the mixture increased from 210° to 250°C. The reaction was completed in one hour. Heating was discontinued and the crude oil was allowed to cool to room temperature before being diluted to twice its volume with heptane.

5 The oil was extracted with two portions of saturated sodium chloride, followed by extraction with several portions of isopropanol/methanol/water. Volatiles were stripped from the oil under vacuum (178.54 g oil recovered).

10 The oil was extracted with two portions of saturated sodium chloride, followed by extraction with several portions of isopropanol/methanol/water. Volatiles were stripped from the oil under vacuum (178.54 g oil recovered).

15 The next examples, 21 and 22, illustrate the lipase hydrolysis testing and the results of the feeding tests for the low calorie oils.

20 Example 21 - Lipase Test Trials

The polyglycerol oils were submitted to a lipase assay, which has been used as a screening test for feeding studies.

25 Lipase Assay

Principle

A stabilized test oil emulsion is incubated with lipase and buffer of pH 8.0 overnight. The test oil is hydrolyzed by lipase to fatty acids, diglycerides and to a small extent monoglycerides and glycerol. The fatty acids liberated in the reaction are titrated with 0.050 N NaOH to a pH of 10.5.

Methods

In one 15x45 mm, 4 ml vial are combining the following: 0.5 ml H₂O; 0.5 ml of 7 percent (w/v) gum acacia (gum arabic); 0.5 ml of candidate oil and 0.2 ml of 0.2 M tris buffer pH 8.0 (tris(hydroxymethyl)-aminomethane which can be purchased from Sigma Chemical Co., St. Louis, MO). In practice the water, gum acacia, and buffer are combined into a stock solution (10-20 ml) and a sample of 1.2 ml of this mixture is added to 500 microliters of test oil in the vial. Each test run will contain a sample of olive oil emulsion prepared in the same way which serves as a positive control to determine the activity of the lipase and the effectiveness of the emulsification.

The contents of each vial are then sonicated for no more than ~~5.0~~ cycles (power=4; duty=50 percent) in a Tekmar sonic disrupter (Tekmar Company, Cincinnati, OH) equipped with a standard microtip probe. The probe is wiped between samples with a Kimwipe moistened with EtOH or CHCl₃.

The result is a stable creamy white emulsion. Eight each 135 microliter samples are distributed to 21x70 mm, 16 ml sc vials. The four test vials receive 25 10 uL each of a mixture containing 10 percent w/v of each of the following lipases in deionized water: lipase N, lipase G and lipase D (which can be purchased from Amano International Enzyme Co., Inc., P.O. Box 1000, Troy, Virginia 22974). The blanks receive no enzyme at this stage. All of the vials are capped and incubated at 37°C overnight. The unused lipase stock is 30 also capped and incubated at 37°C overnight. This

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allows any enzymatic reactions which might alter pH to take place.

Tritration

For each day's titration, a fresh one liter batch of 0.05 N NaOH is prepared by diluting 1:10 a 5 100 ml sample of purchased reagent 0.5 N NaOH. The 0.05 N NaOH is also standardized against a 0.1 N HCl sample by titration to pH 7.0. All of these steps ensure the accuracy of the titration data.

10 For each sample of oil, the eight tubes are removed from the 37°C incubator. Each tube receives the addition of a 3/8 inch diameter TFE starburst stirring head (which can be purchased from Fisher Scientific Co.) magnetic stirrer and 4.0 ml of H₂O to increase the 15 volume and allow the pH electrode to be submerged. The four "blank" tubes receive 10 microliters of the overnight incubated lipase stock solution immediately prior to titration.

20 All samples are then titrated to pH 10.5 in a Fisher Computer Aided Tritrimeter equipped with a Gel-Filled Polymer Body Combination pH electrode (which can be purchased from Fisher Scientific Co.). The 25 average number of mls added to the blank sample are subtracted from the average number of ml added to the test sample to determine the mL OH required to neutralize the acid from 50 microliters of oil.

30 From the determined value of density for the oil, a value of lipase liberated milliequivalents of acid per gram of oil is computed. This value is divided by the value for total available acid determined by saponification of a measured mass of test oil. From

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this ratio, a value for percent lipase hydrolysis is computed.

TABLE III
LIPASE TESTS RESULTS

Sample	Made in Example	Percent Lipase Hydrolysis
Propoxylated decaglycerol oil	27	0
Propoxylated decaglycerol oil	25	0
Butoxynonaglycerol oil	18	3
Butoxynonaglycerol oil	19	6
Propoxynonaglycerol oil	17	.5
Octaglycerol decaoleate*	15	.19

*This is an uncapped polyglycerol oil.

Thus, as can be seen in Table III, the polyglycerol oil is not substantially hydrolyzed.

Example 22 - Animal Feedings

Some of oils submitted for lipase testing in Example 21 were submitted for rat feeding studies. For two weeks rats were fed diets containing various levels of test oils.

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TABLE IV
Results From Feeding Studies

	Made in Example	Oil Percent Recovery in Feces
5	Propoxylated decaglycerol oil	27
	Propoxylated decaglycerol oil	25
	Propoxylated Nonaglycerol oil	17
	Butoxynonaglycerol oil	18
	Butoxynonaglycerol oil	19
	Octaglycerol decaoleate*	15

15 *This is an uncapped polyglycerol oil.

Thus, as seen in Table IV, the polyglycerol is not digested in animals.

CAPPING AND ESTERIFYING THE POLYGLYCEROL

20 Example 23 - Synthesis of Propoxylated Polyglycerol

Undecaglycerol (323.14 g, 0.385 mol) was warmed and poured into a 2-liter stainless steel autoclave fitted with a heating coil and a dip tube for subsurface addition. Potassium (1.62 g, 0.041 mol) was added, and the mixture stirred for two hours at 60°C as nitrogen was flushed through the reactor. The mixture was heated to 90°C, the system closed and pressured to 38 psig (365 kPa) with nitrogen. Propylene oxide (428 g, 30 7.38 mol) was pumped into the reactor, a maximum pressure of 84 psig (682 kPa) being recorded. After stirring for ten hours, the nitrogen pressure was released and the hot mixture poured into a rotary evaporator flask. The flask and contents were placed in

-36-

the rotary evaporator and the volatiles stripped, yielding 752.4 g of polymeric material. The polymer was viscous, but less so than the starting polyglycerol. The molecular weight of the polymer is given below.

Mz = 1459
5 Mw = 1409
Mn = 1345
No primary carbinols were detectable in the ^{13}C NMR spectrum.

10 Example 24 - Esterification of the Propoxylated Undecaglycerol Produced in Example 23

A. First Stage - Esterification with Oleic Acid

Propoxylated undecaglycerol (708.2 g, 0.526 mol) was mixed with 2008 g, (7.10 mol) of oleic acid, stirred vigorously in a 5-liter flask under nitrogen for several hours. Approximately 6 mL of phosphoric acid was added to the mixture. The flask was fitted with a Dean-Stark trap with watercooled condenser. Toluene (885 g, total) was added to the flask and trap. p-Toluene sulfonic acid monohydrate (22.8 g, ca 2 mol percent of the oleic acid) was added and the mixture heated to reflux (135°C). After three hours, 75 mL of water had been trapped. The mixture was allowed to cool before it was extracted with 50 percent saturated NaCl solution (twice). Toluene was stripped from the dark mixture under reduced pressure via the rotary evaporator. The residue was diluted with a large portion of hexane, and the solution filtered through fine amorphous silica gel. The filtrate was extracted with a solution made from 10 g of sodium hydroxide dissolved in 200 g of 50 percent saturated

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sodium chloride solution. The hexane was then stripped from the oil.

Based on the volume of water azeotroped, 8 of the 13 available hydroxyls were esterified.

5 B. Second Stage - Esterification With Acetic Anhydride

The crude oil from the procedure above (2064.9 g, est. 0.66 mol) was stirred with 5 g of p-toluene sulfonic acid monohydrate at 70°C as 401.44 g
10 (3.94 mol) of acetic anhydride was added over a 1/2-hour period. The mixture was stirred overnight at 85°C. Water (23 mL) was added to the mixture at 75°C to decompose excess anhydride. The oil was extracted with saturated NaCl solution. Equal volumes of oil and water
15 were mixed in a rotary evaporator flask and the water and volatiles removed under reduced pressure. A slurry was made of the oil with fine amorphous silica gel and the slurry exhaustively extracted with hexane. The hexane was extracted with two 50 mL portions of a
20 solution of 10 g of NaOH in 50 percent saturated NaCl. A sample of the oil was titrated for free fatty acid content. The oil was found to have a Fatty Acid Value (FAV) of 54.54 mg KOH per gram sample (27.4 percent
oleic acid). The oil (1324.1 g) was saturated with
25 anhydrous ethanol and extracted with (12) 300 mL portions of same. The ethanol washes were saved. Ethanol was stripped from the oil on the rotavap
(578.8 g recovered). Titration of a sample indicated
30 that the oil had a FAV of 2.15 (1.08 percent oleic). This oil was not processed further.

The ethanol washes were combined and concentrated on the rotavap. It was found via titration

that the oil recovered from the ethanol contained 55 percent oleic acid. The oil was treated as above to a FAV of 2.25 (1.13 percent oleic).

Example 25 - Synthesis of Propoxylated Decaglycerol

Decaglycerol (283.76 g, 0.376 mol) was stirred 5 in a 2-liter autoclave with 1.45 g (0.0376 mol) of potassium for two hours with nitrogen flush. Over this time period the temperature was raised gradually from 50° to 90°C. The system was closed and propylene oxide 10 was added over a 25-minute period (74.84 g, 1.29 mol). A maximum pressure of 40 psig (380 kPa) was reached, and 15 this pressure dropped to atmospheric pressure over the next 4-1/2-hours. The mixture stirred for an additional two hours at 90°C. The viscous liquid was stripped of volatiles on the rotavap, and samples were analyzed for molecular weight and secondary hydroxyl content.

Mz = 1045
Mw = 980
20 Mn = 903

Primary carbinols were not detectable in the 13C NMR.

Example 26 - Esterification of the Propoxylated Decaglycerol produced in Example 25

A. First Stage - Esterification with Oleic Acid

In a 5-liter round-bottom flask with a Dean-Stark trap and condenser, propoxylated decaglycerol 30 (324 g, 0.360 mol) was stirred vigorously with 1207.94 g (4.28 mol) of oleic acid and 540 g of toluene under a nitrogen atmosphere. The mixture was heated to approximately 100°C and 40.56 g (5 mol percent of oleic acid) of p-toluene sulfonic acid monohydrate was quickly added to the reaction mixture. Refluxing commenced at

-39-

123°C, the temperature equilibrated at 135°C. Water was azeotropically distilled and collected in a Dean-Stark trap; a total of 70 mL was collected. The dark mixture was extracted with 50 percent saturated NaCl solution (twice). The toluene was removed under reduced pressure on the rotary evaporator.

5

The amount of water azeotroped indicated that 10 of 12 hydroxyls were esterified.

10 B. Second Stage - Esterification with Acetic
 Anhydride

15 The crude dark oil prepared in the above procedure (1260.0 g, 0.36 mol) was stirred vigorously with 318.53 g of acetic anhydride (3.12 mol). p-Toluene sulfonic acid monohydrate was added (1.2 g) and the mixture heated to 80°C and stirred for 48 hours. The mixture was cooled and water added. The two-phase mixture was concentrated, volatiles being removed with water during rotary evaporation. The crude product was 20 saturated with ethanol and extracted with a mixture of NaOH (20 g) in ethanol (800 mL)/water (200 mL). The oil was extracted with two 300 mL portions of ethanol, followed by extraction with a solution of NaOH (10 g) in ethanol/water (200 mL/800 mL). Ethanol was removed from 25 the oil under reduced pressure and the dark oil slurried with fine amorphous silica gel. The oil was extracted from the silica gel with hexane. The hexane was filtered and the oil concentrated. The amber oil was steam-stripped by the addition of water followed by its removal under reduced pressure. The oil was analyzed 30 and had a FAV of 2.45 (1.23 percent oleic acid).

Examples 27-30 illustrate the capping of the polyglycerol.

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Example 27 - Nonaglycerol capped with propylene oxide

Nonaglycerol (535.3 g, 0.809 mol) was poured into a 2-liter stainless-steel pressure reactor. Potassium metal (1.59 g, 0.0407 mol) was added and the mixture was stirred while the system was flushed with nitrogen. The temperature of the mixture was raised gradually from 23° to 90°C over a period of four hours. The nitrogen purge was stopped, the vents closed and propylene oxide (140.4 g, 2.42 mol) was pumped, subsurfacially, into the mixture. The pressure inside the reactor dropped from 48 psig to 1 psig over a 2 and 1/2-hour period. The mixture was stirred for an additional 11 hours.

Example 28 - Decaglycerol Capped With Butylene Oxide

Decaglycerol (303 g, 0.416 mol) was poured into a 2-liter stainless-steel reactor. Potassium metal (0.77 g, 0.020 mol) was added and the mixture stirred under an atmosphere of nitrogen. The temperature was raised from 45° to 90°C over a three-hour period. At this temperature, butylene oxide (90 g, 1.25 mol) was added over a 2 and 1/2 hour period. The mixture was stirred for an additional 12 hours. At this point, the pressure inside the reactor was equal to atmospheric pressure.

Example 29 - Decaglycerol Capped With Butylene Oxide

Decaglycerol (269.19 g, 0.376 mol) was stirred with 1.92 g (0.049 mol) of potassium in a 2-liter stainless steel pressure reactor, under nitrogen. The mixture was heated gradually from 40° to 90°C over a three-hour period. Butylene oxide was pumped into the system subsurfacially (85 g, 1.18 mol). The reaction

-41-

mixture was stirred for 15 hours at 92°C. The pressure inside the reactor was equal to atmospheric pressure at this point. Heating was stopped and a sample of the polymer sent for molecular weight analysis ($M_n = 785$). The percent of secondary hydroxyls is 99+.

5 Example 30 - Decaglycerol Capped With Butylene Oxide

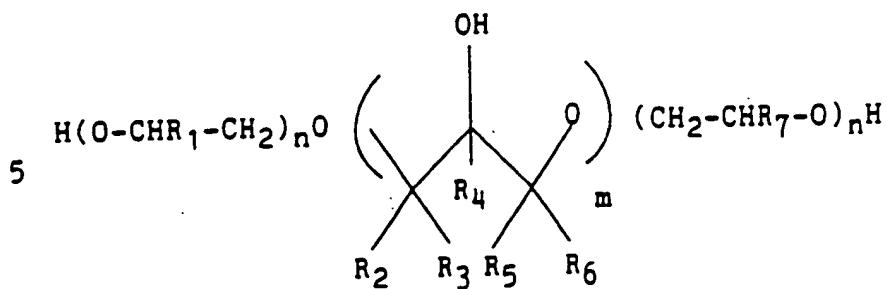
Decaglycerol (303 g, 0.416 mol) was poured into a 2-liter stainless steel pressure reactor. Potassium metal (0.77 g, 0.02 mol) was added and the mixture 10 stirred under nitrogen. The temperature was raised from 45° to 90°C over a three-hour period. At the high temperature butylene oxide was pumped into the reactor, below the surface of the alkoxide mixture (90 g, 15 1.25 mol), over a 2 and 1/2 hour period. The mixture was stirred for 12 hours after complete addition of the butylene oxide. The pressure inside the reactor dropped to zero psig over this period. The polymer was analyzed for molecular weight ($M_n = 802$). The yield of 20 recoverable polyglycerol after transferral was, 391.8g (99.5 percent). The percent of secondary hydroxyls is 99+.

25

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-42-

1. A linear polyglycerol composition characterized in that it corresponds to the formula:



10 where m is an integer from 2 to 30 inclusive, R_1 and R_7 are each independently alkyl groups of 1 to 4 carbon atoms, n is an integer from 0 to 32 inclusive, R_2 , R_3 , R_4 , R_5 and R_6 are each independently hydrogen or an alkyl group having 1 to 3 carbon atoms and the composition is at least 50 weight percent linear polyglycerol moieties and contains less than 20 weight percent of compounds wherein m is 3 or less.

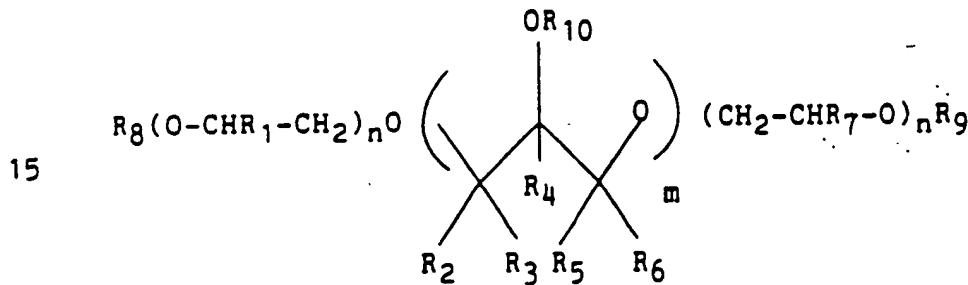
15 20 2. The linear polyglycerol composition as described in Claim 1 wherein m is an integer from 6 to 15; R_1 and R_7 are each independently alkyl groups of 1 to 3 carbon atoms; n is an integer of 1 to 15 inclusive.

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3. The linear polyglycerol composition of
 Claim 1 wherein m is an integer from 8 to 12 inclusive;
⁵ R₁ and R₇ are each independently alkyl groups of 1 or 2
 carbon atoms; n is an integer from 1 to 5 inclusive; and
 said composition containing less than 5 percent
 oligomers.

4. A low caloric oil composition derived from
 a linear polyglycerol as described in Claim 1, 2, or 3,
 said composition corresponding to the formula:

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20 m, R₁, R₇, n, R₂, R₃, R₄, R₅ and R₆ are each as
 previously described and R₈, R₉ and R₁₀ are each
 independently acyl groups having 5 to 23 carbon atoms.

25 5. The low caloric oil of Claim 4, wherein the
 acyl group is derived from the fatty acids present in
 one or more of the following olive oil, soy bean oil,
 coconut oil, palm oil, cotton seed oil and canola oil.

30 6. A method of making a polyglycerol
 composition like that described in Claim 1, comprising:

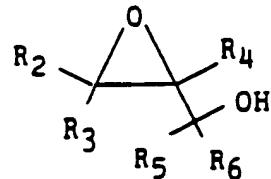
- (a) heating a mixture of a basic catalyst and an initiator with agitation to a temperature of from 25° to 130°C, wherein the initiator is a sugar, sugar

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alcohol, dihydroxy alcohol, polyhydroxy alcohol, polyether polyol, metal alkoxide or metal hydroxide, and

5 (b) adding a monomer to the catalyst and initiator mixture while the temperature of mixture is maintained between 100° to 160°C, wherein the monomer is of the general formula:

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and R₂, R₃, R₄ and R₅ are each independently hydrogen or an alkyl group having 1 to 3 carbon atoms.

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7. The method of Claim 6, wherein the initiator is glycerine, the monomer is glycidol and the catalyst is potassium, potassium hydroxide, sodium, sodium hydroxide, barium hydroxide or calcium hydroxide.

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8. The method of Claim 7, wherein the amount of catalyst heated with the glycerine is 0.5 mole percent to 10 mole percent based on the glycerine present.

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9. The method of Claim 7 further comprising:

(a) mixing the polyglycerol with a catalyst and slowly raising the temperature of the mixture from 20° to 110°C; and

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(b) adding to the mixture an alkylene oxide having 3 to 6 carbon atoms until the vapor pressure decreases to zero.

10. A method of making a low caloric fat substitute comprises esterifying the polyglycerol
5 composition prepared as described in Claim 9 with a fatty acid or fatty acid equivalent.

11. An edible product comprising the low calorie oil composition of Claim 4 or 5.

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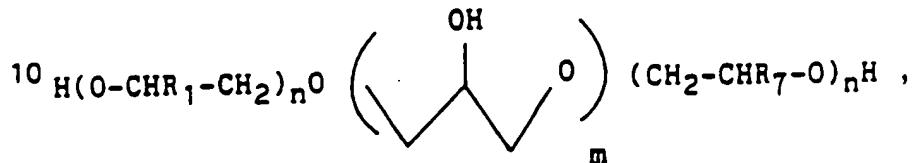
-46-

AMENDED CLAIMS

[received by the International Bureau on 28 March 1991 (28.03.91);
original claims 1-11 replaced by amended claims 1-11 (4 pages)]

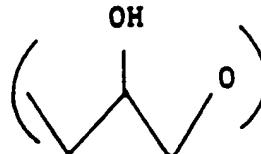
1. A polyglycerol composition made by the method of Claim 6 characterized in that the composition is at least 50 weight percent linear polyglycerol moieties and contains less than 20 weight percent of oligomer compounds.

2. The polyglycerol composition as described in
5 Claim 7 characterized in that it corresponds to the formula



15 wherein m is an integer from 6 to 15; R₁ and R₇ are each independently alkyl groups of 1 to 3 carbon atoms; and the composition is at least 80 weight percent

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units.

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3. The linear polyglycerol composition of
Claim 2 wherein m is an integer from 8 to 12 inclusive;
 R_1 and R_7 are each independently alkyl groups of 1 or 2
carbon atoms; n is an integer from 1 to 5 inclusive; and
said composition contains less than 5 percent oligomers.

5 4. A low caloric oil composition derived from
a polyglycerol as described in Claim 1, 2, or 3,
characterized in that the polyglycerol is esterified
with acyl groups having 5 to 23 carbon atoms.

10 5. The low caloric oil of Claim 4, wherein the
acyl group is derived from the fatty acids present in
one or more of the following olive oil, soy bean oil,
coconut oil, palm oil, cotton seed oil and canola oil.

15 6. A method of making a polyglycerol
composition comprising:

20 (a) heating an initiator in the presence of
a base catalyst with agitation to a
temperature of from 25° to 130°C,
wherein the initiator is a sugar, sugar

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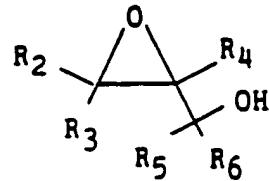
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-48-

alcohol, dihydroxy alcohol, polyhydroxy alcohol, polyether polyol, metal alkoxide or metal hydroxide, and

5 (b) adding a monomer to the initiator mixture while the temperature of mixture is maintained between 100° to 160°C, wherein the monomer is of the general formula:

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15 and R₂, R₃, R₄ and R₅ are each independently hydrogen or an alkyl group having 1 to 3 carbon atoms, and the monomer is added at a rate so as to avoid build-up of unreacted monomer.

20 7. The method of Claim 6, wherein the initiator is glycerine, the monomer is glycidol and the catalyst is potassium, potassium hydroxide, sodium, sodium hydroxide, barium hydroxide or calcium hydroxide.

25 8. The method of Claim 7, wherein the amount of catalyst heated with the glycerine is 0.5 mole percent to 10 mole percent based on the glycerine present.

30 9. The method of Claim 7 further comprising:

(c) mixing the polyglycerol from step (b) with a catalyst and slowly raising the temperature of the mixture from 20° to 110°C; and

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(d) adding to the mixture an alkylene oxide having 3 to 6 carbon atoms until the oxide vapor pressure decreases to zero.

10. A method of making a low caloric fat substitute comprises esterifying the polyglycerol
5 composition prepared as described in Claim 6, 7, 8 or 9 with a fatty acid or fatty acid equivalent.

11. An edible product comprising the low calorie oil composition of Claim 4 or 5.

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US91/00260

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5) : A23D 7/00, 9/00

U.S. CL : 426/601

II. FIELDS SEARCHED

Minimum Documentation Searched *

Classification System	Classification Symbols
U.S.	426/601, 602, 603, 611

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched *

III. DOCUMENTS CONSIDERED TO BE RELEVANT **

Category *	Citation of Document, * with indication, where appropriate, of the relevant passages ***	Relevant to Claim No. 6
Y	US,A 4,861,613 (WHITE ET AL) 29 August 1989 See Abstract and Claims 1-13.	1-11
Y	BABAYAN, V.K., "POLYGLYCEROL ESTERS: UNIQUE ADDITIVES FOR THE BAKERY INDUSTRY," Cereal Foods World, October 1982, Vol. 27, No. 10, pages 510-512, See the entire article.	1-11

* Special categories of cited documents: **

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

IV. CERTIFICATE

Date of the Actual Completion of the International Search *

12 FEBRUARY 1991

Date of Mailing of this International Search Report *

04 MAR 1991

International Searching Authority *

ISA/US

Signature of Authorized Officer *Leslie Wood* *Nguyen Ngoc Ho*

LESLIE WOOD

INTERNATIONAL DIVISION